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(30) Priority:	(71) Applicant: <b>HITACHI LTD</b>
(43) Date of application publication: <b>06.10.00</b>	(72) Inventor: <b>OKUMURA SOUBUN HONBO MICHIKO</b>
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**(54) LITHIUM SECONDARY BATTERY**

(57) Abstract:

**PROBLEM TO BE SOLVED:** To provide a secondary battery having battery characteristics that do not decrease and being excellent in safety such that explosion and firing are prevented even in the event of breakdown due to an internal short circuit or overcharging.

**SOLUTION:** This lithium secondary battery, including positive and negative electrodes which reversibly store and release lithium and an electrolyte containing lithium ions, contains an oxygen absorber. The oxygen absorber is preferably heat polymerizable and is preferably a polysiloxane compound or phenylene oxide compound which absorbs and polymerizes oxygen desorbed from the electrodes. The lithium ion secondary battery having enhanced safety for battery breaking tests can thus be obtained.

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(57)【要約】(修正有)

【課題】電池特性を低下させず、かつ、内部短絡破壊時や過充電時においても破裂発火の起こらない、安全性に優れた二次電池の提供。

【解決手段】リチウムを可逆的に吸蔵放出する正極と負極及びリチウムイオンを含む電解液を具備するリチウム二次電池において、酸素吸収剤を含有する。酸素吸収剤は熱重合するものが好ましく、特に電極より脱離した酸素を吸収し高分子化するもので、ポリシロキサン系化合物やフェニレンオキシド系化合物が好ましい。

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【特許請求の範囲】

【請求項1】リチウムを可逆的に吸蔵放出する正極と負極及びリチウムイオンを含む電解液を具備するリチウム二次電池において、酸素吸収剤を含有する事を特徴とする二次電池。

【請求項2】前記酸素吸収剤が熱重合する請求項1記載のリチウム二次電池。

【請求項3】前記酸素吸収剤が電極より脱離した酸素を重合開始剤とする請求項1記載のリチウム二次電池。

【請求項4】前記酸素吸収剤が酸素を吸収し高分子化することを特徴とする請求項1記載のリチウム二次電池。

【請求項5】前記酸素吸収剤が図1に示す構造式を有するポリシロキサン系化合物であり、好ましくは重合度3から9であることを特徴とする請求項1記載のリチウム二次電池。ただし図1においてR1, R2は、水素もしくは炭素数1から50の有機官能基を示す。

【請求項6】前記酸素吸収剤が図2に示す構造式を有するフェニレンオキシド系化合物であることを特徴とする請求項1記載のリチウム二次電池。ただし図2においてR1, R2は、水素もしくは炭素数1から50の有機官能基を示す。

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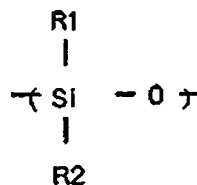
(54) 【発明の名称】 リチウム二次電池

(57) 【要約】 (修正有)

【課題】 電池特性を低下させず、かつ、内部短絡破壊時や過充電時においても破裂発火の起こらない、安全性に優れた二次電池の提供。

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図 1





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## 【特許請求の範囲】

【請求項1】リチウムを可逆的に吸蔵放出する正極と負極及びリチウムイオンを含む電解液を具備するリチウム二次電池において、酸素吸収剤を含有することを特徴とする二次電池。

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【請求項3】前記酸素吸収剤が電極より脱離した酸素を重合開始剤とする請求項1記載のリチウム二次電池。

【請求項4】前記酸素吸収剤が酸素を吸収し高分子化することを特徴とする請求項1記載のリチウム二次電池。

【請求項5】前記酸素吸収剤が図1に示す構造式を有するポリシロキサン系化合物であり、好ましくは重合度3から9であることを特徴とする請求項1記載のリチウム二次電池。ただし図1においてR1、R2は、水素もしくは炭素数1から50の有機官能基を示す。

【請求項6】前記酸素吸収剤が図2に示す構造式を有するフェニレンオキシド系化合物であることを特徴とする請求項1記載のリチウム二次電池。ただし図2においてR1、R2は、水素もしくは炭素数1から50の有機官能基を示す。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、携帯電話やノート型パソコン等のポータブル機器、電気自動車の駆動電源、電力貯蔵用電源に用いるに好適な安全性に優れたリチウム二次電池に関する。

【0002】

【従来の技術】近年、二次電池はパソコンや携帯電話などの電源として、あるいは電気自動車や電力貯蔵用の電源として、なくてはならない重要な構成要素の一つとなっている。

【0003】携帯型コンピュータ（ペンコンピュータと呼ばれるものも含む）や携帯情報端末（Personal Digital Assistant、あるいはPersonal Intelligent Communicator、あるいはハンドヘルド・コミュニケーター）といった移動体通信（モバイル・コンピューティング）が必要とされる要求事項として、小型化、軽量化が挙げられる。しかし、液晶表示パネルのバックライトや画面制御によって消費される電力が高いことや、二次電池の容量が現状ではまだ不十分であることなどの点から、システムのコンパクト化、軽量化が難しい状況にある。

【0004】さらに、地球環境問題の高まりとともに排ガスや騒音を出さない電気自動車が関心を集めている。しかし、現状の電池ではエネルギー密度、出力密度が低いことから走行距離が短い、加速性が悪い、車内のスペースが狭い、車体の安定性が悪いなどの問題点が生じている。二次電池の中でも特に高エネルギー密度が実現できるリチウム二次電池は、従来の鉛蓄電池あるいはニッケルカドミウム電池の代替電池として、最近盛んに研究開

発が進められている。

【0005】しかしながら、このようなリチウム二次電池では、過充電、加熱、短絡などの安全性に関しては問題が多い。リチウム二次電池は、可燃性の有機溶媒を主とする非水電解液を用いているため、電池への釘さしや圧壊といった内部短絡破壊時あるいは過充電時には、正極活性物質が発熱分解し非水電解液に着火すると発熱暴走反応となり、電池が破裂発火に至る。

【0006】そのため、従来このような危険性を回避する方法として、さまざまな対策が提案されている。例えば、電解液に添加剤を含有させ電解液の安全性を改善する技術としては、自己消化性のあるリン酸エステル類を含有させる技術（特開平4-184870号公報）、電解液に自己消化性のあるハロゲン原子置換リン酸エステル化合物を含有させる技術（特開平8-88023号公報）、難燃剤または電解液硬化反応を起こす化学物質を含有したマイクロカプセルを含有させる技術（特開平6-283206号公報）、あるいはラジカル捕捉剤を含有させる技術（特開平10-154531）が開示されている。また、電解液そのものにおいて、フッ素置換化合物（特開平7-312277号公報）や塩素置換化合物（特開平8-45544号公報）を用いることで、引火点を高くして安全性を確保する技術が提案されている。

【0007】

【発明が解決しようとする課題】しかしながら、上記の自己消化性のある物質や、引火点の高い物質を電解液に含有させると、電解液のイオン伝導度が低下するため、電池の高率放電特性や低温特性が低下してしまう。また、難燃剤または電解液硬化反応を起こす化学物質を含有したマイクロカプセルを含有させる技術を用いても、内部短絡破壊時あるいは過充電時に電極より放出される酸素により電解液の燃焼が加速され、破裂発火に至るため安全性の面で充分な特性とは言い難い。またラジカル捕捉剤を含有させる技術を用いても、電池製造時に電池内に取り込まれる酸素によりラジカル捕捉剤が消費されるほか、ラジカル捕捉剤自身が電極と反応するため電池特性が低下するといった問題点がある。

【0008】本発明が解決しようとする課題は、電池特性を低下させず、かつ、内部短絡破壊時や過充電時においても破裂発火の起こらない、安全性に優れた二次電池を提供することにある。

【0009】

【課題を解決するための手段】本発明の電池は、内部短絡破壊時や過充電時に発生する酸素を吸収し、発生したジュール熱にともない重合もしくは架橋反応が加速される酸素吸収剤を含有することを特徴とする。本発明者らは、電池内に温度が上昇した時に酸素を吸収しながら重合反応あるいは架橋反応などの硬化反応を起こす酸素吸収剤を含有させることによって、異常温度に上昇したときに、電極からの脱離酸素かつ電解液を固化させ電池の





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内部抵抗を高めて、発火や破裂が起きるのを防止できることを見いだした。

【0010】本発明における酸素吸収剤としては酸素を吸収し置合もしくは架橋を行う化合物であれば、特に限定されことなく用いられ、例えば、ポリシロキサン類（好ましくは重合度3から9）、フェニレンオキンド類等が用いられる。

【0011】その例を図1、図2に示す。図1において、R1、R2は、水素もしくは炭素数1から50の有機官能基を示す。

【0012】上記のポリシロキサン類の中でもR1およびR2が、電解液への溶解度の点から極性の高い官能基が好ましく用いられる。また、正極あるいは負極に添加する際には、電極作製時のバインダーや溶媒に合わせて溶けやすしたりあるいは分散しやすくなるように、R1を選択することが好ましい。

【0013】図2においてR1、R2は、水素もしくは炭素数1から50の有機官能基を示す。

【0014】上記のフェニレンオキンド類の中でもR1およびR2が、電解液への溶解度の点から極性の高い官能基が好ましく用いられる。また、正極あるいは負極に添加する際には、電極作製時のバインダーや溶媒に合わせて溶けやすしたりあるいは分散しやすくなるように、R1を選択することが好ましい。

【0015】本発明の酸素吸収剤の添加量としては、添加する電池内部の部位によっても異なるが、電極、電解液、あるいはセパレータに対し重量比で0.1から20%が好適である。

【0016】本発明のリチウム二次電池に使用可能な正極活性物質は、コバルト酸リチウム（ $\text{LiCoO}_2$ ）、ニッケル酸リチウム（ $\text{LiNiO}_2$ ）などの層状化合物、あるいは一価以上の遷移金属を置換したもの、あるいはマンガン酸リチウム（ $\text{Li}_{1-x}\text{Mn}_x\text{O}_2$ （ただし $x=0\sim0.33$ ））、 $\text{LiMnO}_2$ 、 $\text{LiMn}_2\text{O}_4$ 、 $\text{LiMnO}$ ）、銅-リチウム酸化物（ $\text{Li}_2\text{CuO}_2$ ）、あるいは $\text{LiV}_2\text{O}_5$ 、 $\text{LiFe}_2\text{O}_4$ 、 $\text{V}_2\text{O}_5$ 、 $\text{Cu}_2\text{V}_2\text{O}_7$ などのバナジウム酸化物、あるいは化学式 $\text{LiNi}_x\text{M}_x\text{O}$ （ただし、 $M=\text{Co}$ 、 $\text{Mn}$ 、 $\text{Al}$ 、 $\text{Cu}$ 、 $\text{Fe}$ 、 $\text{Mg}$ 、 $\text{B}$ 、 $\text{Ga}$ であり、 $x=0.01\sim0.3$ ）で表わされるNiサイト置換型ニッケル酸リチウム、あるいは化学式 $\text{LiMn}_x\text{M}_x\text{O}_2$ （ただし、 $M=\text{Co}$ 、 $\text{Ni}$ 、 $\text{Fe}$ 、 $\text{Cr}$ 、 $\text{Zn}$ 、 $\text{Ta}$ であり、 $x=0.01\sim0.1$ ）または化学式 $\text{Li}_2\text{Mn}_x\text{MO}_2$ （ただし、 $M=\text{Fe}$ 、 $\text{Co}$ 、 $\text{Ni}$ 、 $\text{Cu}$ 、 $\text{Zn}$ ）で表わされるマンガン複合酸リチウムまたは化学式 $\text{Li}$ の一部をアルカリ土類金属イオンで置換した $\text{LiMn}_x\text{O}_2$ 、ジスルフィド化合物、あるいは $\text{Fe}_2(\text{MoO}_4)_3$ などが挙げられる。

【0017】他方、負極活性物質にはリチウムと合金化可能な金属、例えば $\text{Al}$ 、 $\text{Sn}$ 、 $\text{Si}$ 、 $\text{In}$ 、 $\text{Ga}$ 、 $\text{Mg}$ 、あるいはこれらの合金などがある。これらの金属ま

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たは合金はリチウムと合金化した材料を利用することも可能である。さらに、天然黒鉛、人造黒鉛、炭素繊維、気相成長法炭素繊維、ピッチ系炭素質材料、ニードルコークス、ポリアクリロニトリル系炭素繊維、カーボンブラックなどの炭素質材料、あるいは5員環または6員環の環式炭化水素または環式含酸素有機化合物を熱分解によって合成した非晶質炭素材料、あるいはポリアセン、ポリパラフェニレン、ポリアニリン、ポリアセチレンからなる導電性高分子材料、あるいは $\text{SnO}$ 、 $\text{GeO}_2$ 、 $\text{SnSiO}_3$ 、 $\text{SnSi}_{1-x}\text{O}_{1+x}$ 、 $\text{SnSi}_{1-x}\text{Al}_x\text{B}_x$ 、 $\text{P}_{1-x}\text{O}_{1+x}$ 、 $\text{SnSi}_{1-x}\text{Al}_x\text{B}_x\text{P}_{1-x}\text{O}_{1+x}$ などを含む14族または15族元素の酸化物、あるいはインジウム酸化物、あるいは亜鉛酸化物、あるいは $\text{Li}_2\text{F}$ 、 $\text{eN}_2$ 、あるいは $\text{Fe}_2\text{Si}$ 、 $\text{FeSi}$ 、 $\text{FeSi}_2$ 、 $\text{Mg}_2\text{Si}$ などのケイ化物なども負極活性物質に使用できる。また、本発明は上記の電池活性物質以外にも適用可能であり、負極にリチウム金属シートを用いてもよい。

【0018】リチウム二次電池の使用可能な電解質は、その化学式が $\text{LiPF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiClO}_4$ 、 $\text{LiCF}_3\text{SO}_3$ 、 $\text{LiCF}_3\text{CO}_2$ 、 $\text{LiAsF}_6$ 、 $\text{LiSbF}_6$ 、低級脂肪族カルボン酸リチウムで表記される電解質またはそれらの混合物を用いることができる。

【0019】リチウム二次電池の非水電解液は、上記のリチウム塩を非水電解液用溶媒へ溶解させた溶液が使用される。非水電解液用溶媒の例として、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ビニレンカーボネート、γ-ブチロラクトン、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネート、1,2-ジメトキシエタン、2-メチルテトラヒドロフラン、ジメチルスルフォキシド、1,3-ジオキソラン、ホルムアミド、ジメチルホルムアミド、プロピオン酸メチル、プロピオン酸エチル、リン酸トリエステル、トリメトキシメタン、ジオキソラン、ジエチルエーテル、スルホラン、3-メチル-2-オキサゾリジノン、テトラヒドロフラン、1,2-ジエトキシエタンのうち1種類以上の溶媒からなる有機溶媒、または有機溶媒分子内の水素の一部をハロゲンへ置換した誘導体、または有機溶媒分子内の水素の一部をアルキル基、アルケン基、アルキン基、芳香族基へ置換した誘導体が挙げられる。また、これらの混合物も使用することができる。

【0020】固体電解質を用いる場合は、上で述べたリチウム塩をエチレンオキンド、アクリロニトリル、フッ化ビニリデン、メタクリル酸メチル、ヘキサフルオロプロピレンの高分子に保持させて使用する。

【0021】ゲル状電解液を用いる場合は、エチレンオキンド、アクリロニトリル、フッ化ビニリデン、メタクリル酸メチル、ヘキサフルオロプロピレンの高分子内に、上で列記した非水電解液を保持させて使用する。

【0022】本発明の安全性の高い二次電池の用途は、



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特に限定されないが、例えばパーソナルコンピュータ、大型電子計算機、ノート型パソコン、ペン入力パソコン、ノート型ワープロ、携帯電話、携帯カード、腕時計、カメラ、電気シェーバ、コードレス電話、ファックス、ビデオ、ビデオカメラ、電子手帳、電卓、通信機能付き電子手帳、携帯コピー機、液晶テレビ、電動工具、掃除機、バーチャルリアリティ等の機能を有するゲーム機器、玩具、電動自転車、医療介護用歩行補助機、医療介護用車椅子、医療介護用移動式ベッド、エスカレータ、エレベータ、フォークリフト、ゴルフカート、非常用電源、ロードコンディショナ、電力貯蔵システムなどの電源として使用することが出来る。また、民生用のほか、軍用、宇宙用としても用いることが出来る。

【0023】本発明の非水電解液を用いることにより、電池の内部短絡および過充電に対して安全性の向上したリチウム二次電池が得られる。

【0024】

【発明の実施の形態】以下では、本発明の内容を実施例に基いて詳細に説明する。ただし、本発明は下記の実施例によって何ら限定されることはなく、本発明の主旨

【0025】実施例1

正極活物質として $\text{LiCoO}_2$ 、導電助剤として黒鉛粉末、結着剤としてポリフッ化ビニリデン(PVDF)を用い、それぞれ重量比88%、7%、5%の割合で配合して、溶剤としてN-メチル-2-ピロリドン(NMP)を加え、十分に混合して正極合剤を調製した。この正極合剤を厚みが20 $\mu\text{m}$ のAl箔の片面に塗布して、NMPを乾燥後、ロールプレスで成形して正極シートを作製した。正極作製と同様に、負極活物質として、導電助剤として黒鉛粉末、結着剤としてポリフッ化ビニリデン(PVDF)を用い、それぞれ重量比80%、15%、5%の割合で配合して、溶剤としてN-メチル-2-ピロリドン(NMP)を加え、十分に混合して負極合剤を調製した。この負極合剤を厚みが20 $\mu\text{m}$ のCu箔の片面に塗布して、NMPを乾燥後、ロールプレスで成形して負極シートを作製した。

【0026】セパレータは厚みが25 $\mu\text{m}$ 、直径が18mmのポリエチレン製の微孔膜を用いた。

【0027】電解液は、体積比が1:1のエチレンカーボネートとジエチルカーボネートの混合溶媒に、1mol/L $\text{LiPF}_6$ の電解質を溶解して調整し、これに酸素吸収剤として重合度3のポリジメチルシロキサンを重量比5%の割合で配合することによって調製した。

【0028】正極、セパレータ、負極の順で積層して円筒状に巻き込み、端子を取り付けた。電池缶に収納後、電解液を含浸させて電池蓋をかしめ合わせて直径18mm、高さ65mmの18650円筒型電池を作製した。

【0029】このリチウム二次電池を用いて、充放電電

流3mA、充電終止電圧を4.2V、放電終止電圧を1.5Vに設定して充放電を5回行った。電池は1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電し、1400mAhで2.7Vまで放電する充放電を5回繰り返した。

【0030】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充電容量1400mAhの電池を速さ5mm/secで釘を電池に貫通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0031】比較例1

非水電解液中に酸素吸収剤を添加しないこと以外は、実施例1と同様にして二次電池を作成し、評価した。釘刺し試験および過充電試験では、破裂発火した。

実施例2

重合度3のポリジメチルシロキサンを電解液に添加せず、正極に重量比5%の割合で添加した以外は実施例1と同様に電池を作製して、釘刺し試験および過充電試験を行った。

【0032】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充電容量1400mAhの電池を速さ5mm/secで釘を電池に貫通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0033】実施例3

重合度3のポリジメチルシロキサンを電解液に添加せず、負極に重量比5%の割合で添加した以外は実施例1と同様に電池を作製して、釘刺し試験および過充電試験を行った。

【0034】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充電容量1400mAhの電池を速さ5mm/secで釘を電池に貫通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0035】実施例4

ポリジメチルシロキサンの替わりにポリフェニレンオキシドを、正極に重量比5%の割合で添加した以外は実施例1と同様に電池を作製して、釘刺し試験および過充電試験を行った。

【0036】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充電容量1400mAhの電池を速さ5mm/secで釘を電池に貫通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0037】実施例5

ポリジメチルシロキサンの替わりにポリフェニレンオキ



(5)

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シドを、電解液に重量比5%の割合で添加した以外は実施例1と同様に電池を作製して、釘刺し試験および過充電試験を行った。

【0038】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充電容量1400mAhの電池を速さ5mm/secで釘を電池に通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0039】実施例6

ポリジメチルシロキサンに替わりにポリフェニレンオキシドを、負極に重量比5%の割合で添加した以外は実施例1と同様に電池を作製して、釘刺し試験および過充電試験を行った。

【0040】釘刺し試験では1400mAで4.2Vまで定電流で充電後、4.2Vで3時間定電圧充電した充 \*

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\* 電容量1400mAhの電池を速さ5mm/secで釘を電池に通させた。また、過充電試験では、2800mAの定電流で充電しつづけた。両者とも破裂発火は確認できなかった。

【0041】

【発明の効果】本発明により、電池の破壊試験に対しての安全性の向上したリチウムイオン二次電池が得られる。

【図面の簡単な説明】

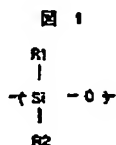
10 【図1】本発明電池に含まれる酸素吸収剤の一例であるポリシロキサンの構造式を示す図である。

【図2】本発明電池に含まれる酸素吸収剤の他の一例であるフェニレンオキシドの構造式を示す図である。

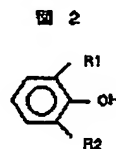
【符号の説明】

R1、R2…水素もしくは炭素数1から50の有機官能基。

【図1】



【図2】



フロントページの続き

Fターム(参考) 5H003 AA10 BB02 BB04 BB05 BB12  
BB13 BB32 BB33 BB35  
5H014 AA06 EE01 EE02 EE03 EE05  
EE08 EE10  
5H029 AJ12 AK03 AL07 AL08 AL11  
AM03 AM04 AM05 AM07 AM16  
BJ02 BJ14 EJ11 EJ12



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CLAIMS

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[Claim(s)]

[Claim 1] The rechargeable battery characterized by containing an oxygen absorbent in the lithium secondary battery possessing the electrolytic solution containing the positive electrode, negative electrode, and lithium ion which carry out occlusion discharge of the lithium in reversible.

[Claim 2] The lithium secondary battery according to claim 1. in which the aforementioned oxygen absorbent carries out thermal polymerization.

[Claim 3] The lithium secondary battery according to claim 1. which makes a polymerization initiator the oxygen from which the aforementioned oxygen absorbent was desorbed from the electrode.

[Claim 4] The lithium secondary battery according to claim 1. characterized by the aforementioned oxygen absorbent absorbing and macromolecule-izing oxygen.

[Claim 5] It is the lithium secondary battery according to claim 1. characterized by for the aforementioned oxygen absorbent being the polysiloxane system compound which has the structure expression shown in drawing 1 , and being polymerization degree 3-9 preferably. However, in drawing 1 , R1. and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

[Claim 6] The lithium secondary battery according to claim 1. characterized by being the phenylene oxide system compound with which the aforementioned oxygen absorbent has the structure expression shown in drawing 2 . However, in drawing 2 , R1. and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the lithium secondary battery excellent in suitable safety to use for the drive power supply of portable devices, such as a cellular phone and a notebook sized personal computer, and an electric vehicle, and the power supply for power storage.

[0002]

[Description of the Prior Art] In recent years, the rechargeable battery is one of the important indispensable components as power supplies, such as a personal computer and a cellular phone, or an electric vehicle and the power supply for power storage.

[0003] A miniaturization and lightweight-ization are mentioned as requirements for which mobile communications (mobile computing), such as a carried type computer (what is called pen computer is included), and a Personal Digital Assistant (Personal Digital Assistant, Personal Intelligent Communicator, or handheld computer communicator), are needed. However, a difficult situation has miniaturization of a system, and lightweight-ization from points, like that the power consumed by the back light of a liquid crystal display panel or drawing control is high, and the present condition of the capacity of a rechargeable battery is still inadequate.

[0004] Furthermore, the electric vehicle which makes neither exhaust gas nor noise with a rise of global environment problems attracts the interest. However, by the present cell, since an energy density and power density are low, troubles, like the stability of the body with the narrow space in the car where acceleration nature with short mileage is bad is bad have arisen. Research and development are briskly furthered recently as the lead accumulator of the former [ lithium secondary battery / which can realize high-energy density also especially in a rechargeable battery ], or an alternative cell of a nickel cadmium NIUMU cell.

[0005] However, there are many problems, concerning safeties, such as overcharge, heating, and a short circuit, with such a lithium secondary battery. Since the nonaqueous electrolyte which is mainly concerned with an inflammable organic solvent is used for the lithium secondary battery, if a positive active material carries out exoergic decomposition at the time of internal short circuit destruction called the \*\*\*\* plain-gauze collapse to a cell, or overcharge and nonaqueous electrolyte is lit, it will become an exoergic runaway reaction and a cell will result in rupture ignition.

[0006] Therefore, various cures are proposed as a method of avoiding such [ conventionally ] danger. for example, the technology (JP,6-283206,A) make the microcapsule containing the chemical which causes the technology (JP,4-184870,A) make phosphoric ester with autolysis nature contain if it considers as the technology of making the electrolytic solution containing an additive and improving the safety of the electrolytic solution, the technology (JP,8-88023,A) make the halogen atom substitution phosphoric-ester compound which has autolysis nature in the electrolytic solution contain, a flame retarder, or an electrolytic-solution hardening reaction contain, or the technology (JP,10-154531,A) make a radical scavenger contain is indicated Moreover, in the electrolytic solution



itself, the technology of making the flash point high and securing safety by using a fluorine substituted compound (JP,7-312227,A) and a chlorination compound (JP,8-45544,A) is proposed.  
[0007]

[Problem(s) to be Solved by the Invention] However, if the electrolytic solution is made to contain the matter with the above-mentioned autolysis nature, and the high matter of the flash point, since the ionic conductivity of the electrolytic solution will fall, the high-rate-discharge property and low-temperature property of a cell will fall. Moreover, even if it uses the technology of making the microcapsule containing the chemical which causes a flame retarder or an electrolytic-solution hardening reaction containing, combustion of the electrolytic solution is accelerated by the oxygen emitted from an electrode at the time of internal short circuit destruction or overcharge, and since it results in rupture ignition, it is hard to call it property sufficient in the field of safety. Moreover, even if it uses the technology of making a radical scavenger containing, a radical scavenger is consumed by the oxygen incorporated in a cell at the time of cell manufacture, and also in order for the radical scavenger itself to react with an electrode, there is a trouble that a cell property falls.

[0008] The technical problem which this invention tends to solve is to offer the rechargeable battery excellent in safety with which a cell property is not reduced and rupture ignition does not take place at the time of internal short circuit destruction and overcharge.

[0009]

[Means for Solving the Problem] The cell of this invention is characterized by containing the oxygen absorbent which absorbs the oxygen generated at the time of internal short circuit destruction and overcharge and by which a polymerization or crosslinking reaction is accelerated in connection with the generated Joule's heat. This invention persons found out that it could prevent that solidify the desorption oxygen and the electrolytic solution from an electrode, raise the internal resistance of a cell, and ignition and rupture occur, when it went up to abnormal temperature by making the oxygen absorbent which causes hardening reactions, such as polymerization reaction or crosslinking reaction, contain, absorbing oxygen when temperature rises in a cell.

[0010] If it is the compound which absorbs oxygen as an oxygen absorbent in this invention, and performs a polymerization or bridge formation, it will be used, without being limited especially, for example, polysiloxanes (preferably polymerization degree 3-9) and phenylene oxides will be used.

[0011] The example is shown in drawing 1 and drawing 2. In drawing 1, R1 and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

[0012] The functional group of the point of the solubility to the electrolytic solution to polarity with R1 and R2 is preferably used also in the above-mentioned polysiloxanes. [ high ] Moreover, in case it adds to a positive electrode or a negative electrode, it is desirable to choose R1 so that it may carry out, or it may be easy to distribute and it may become that it is easy to melt according to the binder and solvent at the time of electrode production.

[0013] In drawing 2, R1 and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

[0014] The functional group of the point of the solubility to the electrolytic solution to polarity with R1 and R2 is preferably used also in the above-mentioned phenylene oxides. [ high ] Moreover, in case it adds to a positive electrode or a negative electrode, it is desirable to choose R1 so that it may carry out, or it may be easy to distribute and it may become that it is easy to melt according to the binder and solvent at the time of electrode production.

[0015] Although it changes as an addition of the oxygen absorbent of this invention also with parts inside the cell to add, it is 0.1 at a weight ratio to an electrode, the electrolytic solution, or separator. 20% of shells is suitable.

[0016] A positive active material usable to the lithium secondary battery of this invention Stratified compounds, such as a cobalt acid lithium ( $\text{LiCoO}_2$ ) and a nickel acid lithium ( $\text{LiNiO}_2$ ), or the thing which replaced the transition metals more than a kind or a manganic acid lithium ( $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  (however,  $x=0-0.33$ ) --)  $\text{LiMnO}_3$ ,  $\text{LiMn}_2\text{O}_3$ ,  $\text{LiMnO}_2$ , a copper-lithium oxide ( $\text{Li}_2\text{CuO}_2$ ),  $\text{LiV}_3\text{O}_8$ ,

LiFe 3O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, and Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub> etc. -- a banazin-san ghost -- [ or ] Or chemical formula LiNi<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub> (however, they are M=Co, and Mn, aluminum, Cu, Fe, Mg, B and Ga) nickel site substitution type nickel acid lithium expressed with x=0.01-0.3, Or chemical formula LiMn<sub>2-x</sub>M<sub>x</sub>O<sub>2</sub> (however, they are M=Co, and nickel, Fe, Cr, Zn and Ta) x=0.01-0.1 or chemical formula Li<sub>2</sub>Mn<sub>3</sub>MO<sub>8</sub> LiMn<sub>2</sub>O<sub>4</sub> which replaced a part of manganese compound acid lithium expressed with however, M=Fe, and (Co, nickel, Cu, Zn) or chemical formula Li with alkaline-earth-metal ion, a disulfide compound, Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, etc. are mentioned.

[0017] On the other hand, a lithium and the metal which can be alloyed, for example, aluminum, Sn, Si, In(s), Ga(s), and Mg, these alloys, etc. are in a negative-electrode active material. These metals or alloys can also use a lithium and the alloyed material. Furthermore, carbonaceous material, such as a natural graphite, an artificial graphite, a carbon fiber, a vapor-growth carbon fiber, pitch system carbonaceous material, a needle coke, a polyacrylonitrile system carbon fiber, and carbon black, Or the amorphous-carbon material which compounded the cyclic hydrocarbon of 5 member rings or 6 member rings, or the ring type oxygenated organic compound by the pyrolysis, Or the poly acene, poly para-phenylene, the poly aniline, the conductive polymer that consists of a polyacethylene, Or the oxide of 14 groups containing SnO, GeO<sub>2</sub>, SnSiO<sub>3</sub>, SnSi 0.5O<sub>1.5</sub>, SnSi0.7aluminum0.1B0.3P0.2O<sub>3.5</sub>, SnSi0.5aluminum0.3B0.3P0.5O<sub>4.15</sub>, etc., or 15 group element or an indium oxide, Or silicides, such as a zincic-acid ghost, Li<sub>3</sub>FeN<sub>2</sub> or Fe<sub>2</sub>Si<sub>3</sub>, FeSi, FeSi<sub>2</sub>, and Mg<sub>2</sub>Si, etc. can be used for a negative-electrode active material. Moreover, this invention can be applied besides the above-mentioned cell active material, and may use a lithium metal sheet for a negative electrode.

[0018] The electrolytes written with LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiCF<sub>3</sub>CO<sub>2</sub>, LiAsF<sub>6</sub> and LiSbF<sub>6</sub>, and a low-grade aliphatic carboxylic-acid lithium or those mixture can be used for the usable electrolyte of a lithium secondary battery. [ the chemical formula ]

[0019] The solution made to dissolve the lithium salt of the above [ the nonaqueous electrolyte of a lithium secondary battery ] in the solvent for nonaqueous electrolyte is used. As an example of the solvent for nonaqueous electrolyte, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyrolactone, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 2-methyl tetrahydrofuran, a dimethyl sulfoxide, 1, 3-dioxolane, a formamide, a dimethylformamide, a methyl propionate, an ethyl propionate, trialkyl phosphate, trimethoxy methane, a dioxolane, diethylether, a sulfolane, 3-methyl-2-oxazolidinone, a tetrahydrofuran, 1, the organic solvent which consists of one or more kinds of solvents among 2-diethoxy ethane, the derivative which replaced a part of hydrogen in an organic-solvent molecule to the halogen, or the derivative which replaced a part of hydrogen in an organic-solvent molecule to the alkyl group, the alkene machine, the alkyne machine, and the aromatic machine is mentioned.

Moreover, such mixture can also be used.

[0020] When using a solid electrolyte, it is used making the lithium salt described in the top hold to the macromolecule of ethylene oxide, acrylonitrile, a fluoride vinylidene, a methyl methacrylate, and hexafluoropropylene.

[0021] When using the gel electrolytic solution, it is used in ethylene oxide, acrylonitrile, a fluoride vinylidene, a methyl methacrylate, and the macromolecule of hexafluoropropylene, making the nonaqueous electrolyte listed in the top hold.

[0022] Although especially the use of the high rechargeable battery of the safety of this invention is not limited For example, a personal computer, a large-sized computer, a notebook sized personal computer, a pen input personal computer, a note type word processor, a cellular phone, a pocket card, a wrist watch, a camera, an electric shaver, a cordless telephone, facsimile, video, a video camera, an electronic notebook, a calculator, an electronic notebook with communication facility, The walk auxiliary machine for game machine machine [ which has functions, such as a pocket copy machine a liquid crystal television a power tool, a cleaner, and a virtual reality, ], toy, electromotive bicycle, and medical care, the wheelchair for medical care, the portable type bed for medical care, an escalator, an

elevator, a fork lift truck, a golf khat, It can be used as power supplies, such as an emergency power source, a load conditioner, and a power storage system. Moreover, it can use also as the object for munitions besides a noncommercial use, and an object for space.

[0023] By using the nonaqueous electrolyte of this invention, the lithium secondary battery which improved to the internal short circuit and surcharge of a cell is obtained.

[0024]

[Embodiments of the Invention] Below, the content of this invention is explained in detail based on an example. However, it writes in addition that this invention can be suitably changed in the range which is not limited at all by the following example and does not change the main point of this invention.

[0025] as example 1 positive active material -- as  $\text{LiCoO}_2$  and an electric conduction assistant -- as a graphite powder and a binder -- a polyvinylidene fluoride (PVDF) -- using -- respectively -- a weight ratio -- 88%, 7%, and 5% -- comparatively -- coming out -- blending -- as a solvent -- a N-methyl-2-pyrrolidone (NMP) -- adding -- enough -- mixing -- a positive electrode -- the mixture was prepared this positive electrode -- the mixture was applied to one side of aluminum foil whose thickness is 20 micrometers, was fabricated by the roll press after drying NMP, and the positive-electrode sheet was produced positive-electrode production -- the same -- as a negative-electrode active material -- as an electric conduction assistant -- as a graphite powder and a binder -- a polyvinylidene fluoride (PVDF) -- using -- respectively -- a weight ratio -- 80%, 15%, and 5% -- comparatively -- coming out -- blending -- as a solvent -- a N-methyl-2-pyrrolidone (NMP) -- adding -- enough -- mixing -- a negative electrode -- the mixture was prepared this negative electrode -- the mixture was applied to one side of Cu foil whose thickness is 20 micrometers, was fabricated by the roll press after drying NMP, and the negative-electrode sheet was produced

[0026] As for separator, thickness used the micropore film made from polyethylene 25 micrometers and whose diameter are 18mm.

[0027] the electrolytic solution -- a volume ratio -- the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 -- the electrolyte of 1 mol/LiPF<sub>6</sub> -- dissolving -- adjusting -- this -- as an oxygen absorbent -- the poly dimethylsiloxane of polymerization degree 3 -- a weight ratio -- it prepared by 5% of thing which it comes out comparatively and is blended

[0028] The laminating was carried out in the order of a positive electrode, separator, and a negative electrode, it involved in in the shape of a cylinder, and the terminal was attached. After containing with a cell can, the electrolytic solution was infiltrated, the cell lid was closed and 18650 cylindrical cells with a diameter [ of 18mm ] and a height of 65mm were produced.

[0029] This lithium secondary battery is used and it is 1.5V about 4.2V and a discharge final voltage in 3mA of charge and discharge currents, and charge final voltage. It set up and charge and discharge were performed 5 times. The cell repeated the charge and discharge which carry out constant-potential charge after charge by the constant current to 4.2V by 1400mA 4.2V for 3 hours, and discharge to 2.7V by 1400mAh 5 times.

[0030] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0031] The rechargeable battery was created and evaluated like the example 1 except not adding an oxygen absorbent in example of comparison 1 nonaqueous electrolyte. It \*\*\*\*(ed) and rupture ignition was carried out in the examination and the overcharge examination.

Except having not added the poly dimethylsiloxane of example 2 polymerization degree 3 to the electrolytic solution, but having added at a rate of 5% of heavy quantitative ratios to the positive electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0032] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential

charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours  
Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0033] Except having not added the poly dimethylsiloxane of example 3 polymerization degree 3 to the electrolytic solution, but having added at a rate of 5% of heavy quantitative ratios to the negative electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0034] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours  
Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0035] Instead of example 4 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the positive electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0036] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours  
Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0037] Instead of example 5 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the electrolytic solution, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0038] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours  
Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0039] Instead of example 6 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the negative electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0040] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours  
Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0041]

[Effect of the Invention] The rechargeable lithium-ion battery which improved by this invention is obtained.

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[Translation done.]

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TECHNICAL FIELD

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[The technical field to which invention belongs] this invention relates to the lithium secondary battery excellent in suitable safety to use for the drive power supply of portable devices, such as a cellular phone and a notebook sized personal computer, and an electric vehicle, and the power supply for power storage.

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## PRIOR ART

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[Description of the Prior Art] In recent years, the rechargeable battery is one of the important indispensable components as power supplies, such as a personal computer and a cellular phone, or an electric vehicle and the power supply for power storage.

[0003] A miniaturization and lightweight-ization are mentioned as requirements for which mobile communications (mobile computing), such as a carried type computer (what is called pen computer is included), and a Personal Digital Assistant (Personal Digital Assistant, Personal Intelligent Communicator, or handheld computer communicator), are needed. However, a difficult situation has miniaturization of a system, and lightweight-ization from points, like that the power consumed by the back light of a liquid crystal display panel or drawing control is high, and the present condition of the capacity of a rechargeable battery is still inadequate.

[0004] Furthermore, the electric vehicle which makes neither exhaust gas nor noise with a rise of global environment problems attracts the interest. However, by the present cell, since an energy density and power density are low, troubles, like the stability of the body with the narrow space in the car where acceleration nature with short mileage is bad is bad have arisen. Research and development are briskly furthered recently as the lead accumulator of the former [ lithium secondary battery / which can realize high-energy density also especially in a rechargeable battery ], or an alternative cell of a nickel cadmium NIUMU cell.

[0005] However, there are many problems, concerning safeties, such as overcharge, heating, and a short circuit, with such a lithium secondary battery. Since the nonaqueous electrolyte which is mainly concerned with an inflammable organic solvent is used for the lithium secondary battery, if a positive active material carries out exoergic decomposition at the time of internal short circuit destruction called the \*\*\*\* plain-gauze collapse to a cell, or overcharge and nonaqueous electrolyte is lit, it will become an exoergic runaway reaction and a cell will result in burst ignition.

[0006] Therefore, various cures are proposed as a method of avoiding such [ conventionally ] danger. For example, it is technology of making the electrolytic solution containing an additive and improving the safety of the electrolytic solution. The technology (JP,6-283206,A) make the microcapsule containing the chemical which causes the technology (JP,4-184870,A) make phosphoric ester with autolysis nature contain, the technology (JP,8-88023,A) make the halogen atom substitution phosphoric-ester compound which has autolysis nature in the electrolytic solution contain, a flame retarder, or an electrolytic-solution hardening reaction contain, or the technology (JP,10-154531,A) make a radical scavenger contain are indicated. Moreover, in the electrolytic solution itself, the technology of making the flash point high and securing safety by using a fluorine substituted compound (JP,7-312227,A) and a chlorination compound (JP,8-45544,A) is proposed.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] The rechargeable lithium-ion battery which improved by this invention is obtained.

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[Translation done.]

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] However, if the electrolytic solution is made to contain the matter with the above-mentioned autolysis nature, and the high matter of the flash point, since the ionic conductivity of the electrolytic solution will fall, the high-rate-discharge property and low-temperature property of a cell will fall. Moreover, even if it uses the technology of making the microcapsule containing the chemical which causes a flame retarder or an electrolytic-solution hardening reaction containing, combustion of the electrolytic solution is accelerated by the oxygen emitted from an electrode at the time of internal short circuit destruction or overcharge, and since it results in burst ignition, it is hard to call it property sufficient in the field of safety. Moreover, even if it uses the technology of making a radical scavenger containing, a radical scavenger is consumed by the oxygen incorporated in a cell at the time of cell manufacture, and also in order for the radical scavenger itself to react with an electrode, there is a trouble that a cell property falls.

[0008] The technical problem which this invention tends to solve is to offer the rechargeable battery excellent in safety with which a cell property is not reduced and burst ignition does not take place at the time of internal short circuit destruction and overcharge.

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## MEANS

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[Means for Solving the Problem] The cell of this invention is characterized by containing the oxygen absorbent which absorbs the oxygen generated at the time of internal short circuit destruction and overcharge and by which a polymerization or crosslinking reaction is accelerated in connection with the generated Joule's heat. This invention persons found out that it could prevent that solidify the desorption oxygen and the electrolytic solution from an electrode, raise the internal resistance of a cell, and ignition and rupture occur, when it went up to abnormal temperature by making the oxygen absorbent which causes hardening reactions, such as polymerization reaction or crosslinking reaction, contain, absorbing oxygen when temperature rises in a cell.

[0010] If it is the compound which absorbs oxygen as an oxygen absorbent in this invention, and performs a polymerization or bridge formation, it will be used, without being limited especially, for example, polysiloxanes (preferably polymerization degree 3-9) and phenylene oxides will be used.

[0011] The example is shown in drawing 1 and drawing 2. In drawing 1, R1 and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

[0012] The functional group of the point of the solubility to the electrolytic solution to polarity with R1 and R2 is preferably used also in the above-mentioned polysiloxanes. [ high ] Moreover, in case it adds to a positive electrode or a negative electrode, it is desirable to choose R1 so that it may carry out, or it may be easy to distribute and it may become that it is easy to melt according to the binder and solvent at the time of electrode production.

[0013] In drawing 2, R1 and R2 show hydrogen or the organic functional group of carbon numbers 1-50.

[0014] The functional group of the point of the solubility to the electrolytic solution to polarity with R1 and R2 is preferably used also in the above-mentioned phenylene oxides. [ high ] Moreover, in case it adds to a positive electrode or a negative electrode, it is desirable to choose R1 so that it may carry out, or it may be easy to distribute and it may become that it is easy to melt according to the binder and solvent at the time of electrode production.

[0015] Although it changes as an addition of the oxygen absorbent of this invention also with parts inside the cell to add, it is 0.1 at a weight ratio to an electrode, the electrolytic solution, or separator. 20% of shells is suitable.

[0016] A positive active material usable to the lithium secondary battery of this invention Stratified compounds, such as a cobalt acid lithium ( $\text{LiCoO}_2$ ) and a nickel acid lithium ( $\text{LiNiO}_2$ ), or the thing which replaced the transition metals more than a kind or a manganic acid lithium ( $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  (however,  $x=0-0.33$ ) --)  $\text{LiMnO}_3$ ,  $\text{LiMn}_2\text{O}_3$ ,  $\text{LiMnO}_2$ , a copper-lithium oxide ( $\text{Li}_2\text{CuO}_2$ ),  $\text{LiV}_3\text{O}_8$ ,  $\text{LiFe}_3\text{O}_4$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Cu}_2\text{V}_2\text{O}_7$  etc. -- a banazin-san ghost -- [ or ] Or chemical formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (however, they are  $\text{M}=\text{Co}$ , and  $\text{Mn}$ , aluminum, Cu, Fe, Mg, B and Ga) nickel site substitution type nickel acid lithium expressed with  $x=0.01-0.3$ , Or chemical formula  $\text{LiMn}_{2-x}\text{M}_x\text{O}_2$  (however, they are  $\text{M}=\text{Co}$ , and nickel, Fe, Cr, Zn and Ta)  $x=0.01-0.1$  or chemical formula  $\text{Li}_2\text{Mn}_3\text{MO}_8$   $\text{LiMn}_2\text{O}_4$  which replaced a part of manganese compound acid lithium expressed with however,  $\text{M}=\text{Fe}$ , and (Co, nickel, Cu, Zn) or chemical formula Li with alkaline-earth-metal ion, a disulfide compound,  $\text{Fe}_2(\text{MoO}_4)_3$ , etc. are mentioned.

[0017] On the other hand, a lithium and the metal which can be alloyed, for example, aluminum, Sn, Si, In(s), Ga(s), and Mg, these alloys, etc. are in a negative-electrode active material. These metals or alloys can also use a lithium and the alloyed material. Furthermore, carbonaceous material, such as a

natural graphite, an artificial graphite, a carbon fiber, a vapor-growth carbon fiber, pitch system carbonaceous material, a needle coke, a polyacrylonitrile system carbon fiber, and carbon black, Or the amorphous-carbon material which compounded the cyclic hydrocarbon of 5 member rings or 6 member rings, or the ring type oxygenated organic compound by the pyrolysis, Or the poly acene, poly para-phenylene, the poly aniline, the conductive polymer that consists of a polyacethylene, Or the oxide of 14 groups containing SnO, GeO<sub>2</sub>, SnSiO<sub>3</sub>, SnSi 0.5O<sub>1.5</sub>, SnSi0.7aluminum0.1B0.3P0.2O<sub>3.5</sub>, SnSi0.5aluminum0.3B0.3P0.5O<sub>4.15</sub>, etc., or 15 group element or an indium oxide, Or silicides, such as a zincic-acid ghost, Li<sub>3</sub>FeN<sub>2</sub> or Fe<sub>2</sub>Si<sub>3</sub>, FeSi, FeSi<sub>2</sub>, and Mg<sub>2</sub>Si, etc. can be used for a negative-electrode active material. Moreover, this invention can be applied besides the above-mentioned cell active material, and may use a lithium metal sheet for a negative electrode.

[0018] The electrolytes written with LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiCF<sub>3</sub>CO<sub>2</sub>, LiAsF<sub>6</sub> and LiSbF<sub>6</sub>, and a low-grade aliphatic carboxylic-acid lithium or those mixture can be used for the usable electrolyte of a lithium secondary battery. [ the chemical formula ]

[0019] The solution made to dissolve the lithium salt of the above [ the nonaqueous electrolyte of a lithium secondary battery ] in the solvent for nonaqueous electrolyte is used. As an example of the solvent for nonaqueous electrolyte, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyrolactone, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 2-methyl tetrahydrofuran, a dimethyl sulfoxide, 1, 3-dioxolane, a formamide, a dimethylformamide, a methyl propionate, an ethyl propionate, trialkyl phosphate, trimethoxy methane, a dioxolane, diethylether, a sulfolane, 3-methyl-2-oxazolidinone, a tetrahydrofuran, 1, the organic solvent which consists of one or more kinds of solvents among 2-diethoxy ethane, the derivative which replaced a part of hydrogen in an organic-solvent molecule to the halogen, or the derivative which replaced a part of hydrogen in an organic-solvent molecule to the alkyl group, the alkene machine, the alkyne machine, and the aromatic machine is mentioned. Moreover, such mixture can also be used.

[0020] When using a solid electrolyte, it is used making the lithium salt described in the top hold to the macromolecule of ethylene oxide, acrylonitrile, a fluoride vinylidene, a methyl methacrylate, and hexafluoropropylene.

[0021] When using the gel electrolytic solution, it is used in ethylene oxide, acrylonitrile, a fluoride vinylidene, a methyl methacrylate, and the macromolecule of hexafluoropropylene, making the nonaqueous electrolyte listed in the top hold.

[0022] Although especially the use of the high rechargeable battery of the safety of this invention is not limited For example, a personal computer, a large-sized computer, a notebook sized personal computer, a pen input personal computer, a note type word processor, a cellular phone, a pocket card, a wrist watch, a camera, an electric shaver, a cordless telephone, facsimile, video, a video camera, an electronic notebook, a calculator, an electronic notebook with communication facility, The walk auxiliary machine for game machine machine [ which has functions, such as a pocket copy machine a liquid crystal television a power tool, a cleaner, and a virtual reality, ], toy, electromotive bicycle, and medical care, the wheelchair for medical care, the portable type bed for medical care, an escalator, an elevator, a fork lift truck, a golf cart, It can be used as power supplies, such as an emergency power source, a load conditioner, and a power storage system. Moreover, it can use also as the object for munitions besides a noncommercial use, and an object for space.

[0023] By using the nonaqueous electrolyte of this invention, the lithium secondary battery which improved to the internal short circuit and surcharge of a cell is obtained.

[0024]

[Embodiments of the Invention] Below, the contents of this invention are explained in detail based on an example. However, it writes in addition that this invention can be suitably changed in the range which is not limited at all by the following example and does not change the main point of this invention.

[0025] as example 1 positive active material -- as LiCoO<sub>2</sub> and an electric conduction assistant -- as a graphite powder and a binder -- a polyvinylidene fluoride (PVDF) -- using -- respectively -- a weight ratio -- 88%, 7%, and 5% -- comparatively -- coming out -- blending -- as a solvent -- a N-methyl-2-

pyrrolidone (NMP) -- adding -- enough -- mixing -- a positive electrode -- the mixture was prepared this positive electrode -- the mixture was applied to one side of aluminum foil whose thickness is 20 micrometers, was fabricated by the roll press after drying NMP, and the positive-electrode sheet was produced positive-electrode production -- the same -- as a negative-electrode active material -- as an electric conduction assistant -- as a graphite powder and a binder -- a polyvinylidene fluoride (PVDF) -- using -- respectively -- a weight ratio -- 80%, 15%, and 5% -- comparatively -- coming out -- blending -- as a solvent -- a N-methyl-2-pyrrolidone (NMP) -- adding -- enough -- mixing -- a negative electrode -- the mixture was prepared this negative electrode -- the mixture was applied to one side of Cu foil whose thickness is 20 micrometers, was fabricated by the roll press after drying NMP, and the negative-electrode sheet was produced

[0026] As for separator, thickness used the micropore film made from polyethylene 25 micrometers and whose diameter are 18mm.

[0027] the electrolytic solution -- a volume ratio -- the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 -- the electrolyte of 1 mol/LiPF<sub>6</sub> -- dissolving -- adjusting -- this -- as an oxygen absorbent -- the poly dimethylsiloxane of polymerization degree 3 -- a weight ratio -- it prepared by 5% of thing which it comes out comparatively and is blended

[0028] The laminating was carried out in the order of a positive electrode, separator, and a negative electrode, it involved in in the shape of a cylinder, and the terminal was attached. After containing with a cell can, the electrolytic solution was infiltrated, the cell lid was closed and 18650 cylindrical cells with a diameter [ of 18mm ] and a height of 65mm were produced.

[0029] This lithium secondary battery is used and it is 1.5V about 4.2V and a discharge final voltage in 3mA of charge and discharge currents, and charge final voltage. It set up and charge and discharge were performed 5 times. The cell repeated the charge and discharge which carry out constant-potential charge after charge by the constant current to 4.2V by 1400mA 4.2V for 3 hours, and discharge to 2.7V by 1400mAh 5 times.

[0030] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked burst ignition.

[0031] The rechargeable battery was created and evaluated like the example 1 except not adding an oxygen absorbent in example of comparison 1 nonaqueous electrolyte. It \*\*\*\*(ed) and burst ignition was carried out in the examination and the overcharge examination.

Except having not added the poly dimethylsiloxane of example 2 polymerization degree 3 to the electrolytic solution, but having added at a rate of 5% of heavy quantitative ratios to the positive electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0032] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked burst ignition.

[0033] Except having not added the poly dimethylsiloxane of example 3 polymerization degree 3 to the electrolytic solution, but having added at a rate of 5% of heavy quantitative ratios to the negative electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0034] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0035] Instead of example 4 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the positive electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0036] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours

Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked rupture ignition.

[0037] Instead of example 5 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the electrolytic solution, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0038] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours

Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked burst ignition.

[0039] Instead of example 6 poly dimethylsiloxane, except having added the polyphenylene oxide at a rate of 5% of heavy quantitative ratios to the negative electrode, the cell was produced and \*\*\*\*(ed) like the example 1 and the examination and the overcharge examination were performed.

[0040] It is the cell of charge capacity 1400mAh which it \*\*\*\*(ed) and carried out constant-potential charge after charge by the constant current to 4.2V by 1400mA by examination 4.2V for 3 hours

Speed 5 mm/sec The cell was made to penetrate a nail. Moreover, by overcharge examination, it continued charging by the 2800mA constant current. Both have not checked burst ignition.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the structure expression of the polysiloxane which is an example of the oxygen absorbent contained in this invention cell.

[Drawing 2] It is drawing showing the structure expression of the phenylene oxide which are other examples of the oxygen absorbent contained in this invention cell.

[Description of Notations]

R1, R2 -- Hydrogen or organic functional group of carbon numbers 1-50.

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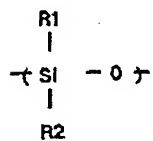
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DRAWINGS

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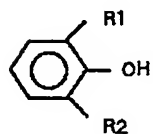
[Drawing 1]

図 1



[Drawing 2]

図 2



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